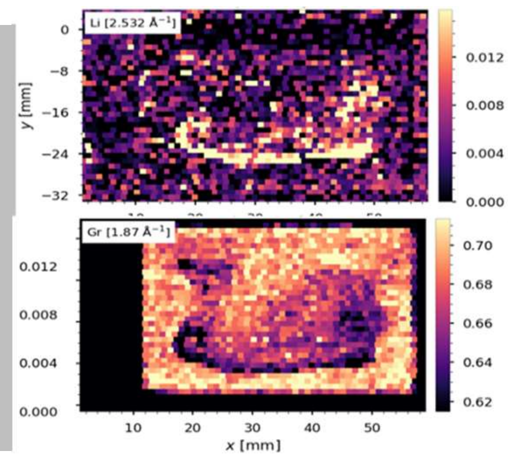
Project ID BAT384

BAT384: APPROACHES TO DETECTING Li DEPOSITION DURING FAST CHARGE



MICHAEL F TONEY
SLAC National Accelerator Laboratory
DANIEL ABRAHAM
Argonne National Laboratory

Other Major Contributors:
Donal Finegan (NREL), **Dan Steingart** (Princeton), **Nitash Balsara & Bryan McCloskey** (LBNL), **Johanna Nelson Weker & Hans Georg-Steinrück** (SLAC)

June 12, 2019
AMR Arlington, VA

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 37%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

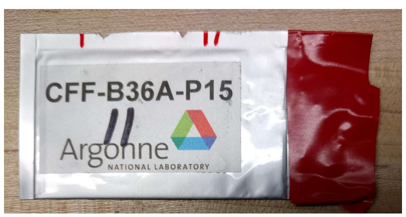
- Funding for FY19 – 6390k
  - ANL – 2400k
  - NREL – 1600K
  - INL – 440K
  - SLAC – 1000K
  - LBNL – 950K

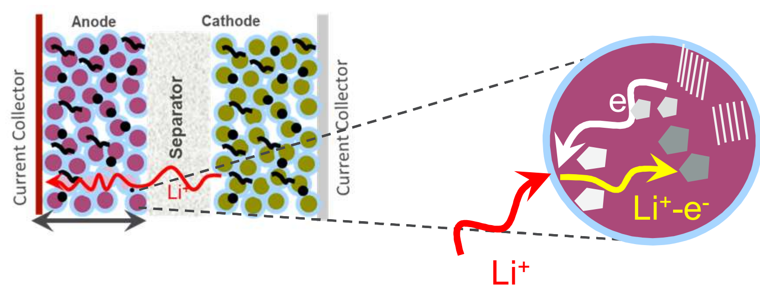
Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab

RELEVANCE

- **Fast charge is major issue impacting widespread adoption of EVs**
- **Better understand what limits fast charging**
  - Li plating is a critical issue limiting fast charge
- **Develop methods to directly detect and characterize (space and time) Li metal plating during fast charging**
- **Understand what cell factors (graphite, electrolyte, …) impact tendency for Li plating**
- **Apply Li-detection methodologies within XCEL**
- **Challenges: fast (few seconds), heterogeneous (2D, 3D, cm - <µm (?)), aggressive environments, "buried" interface,**



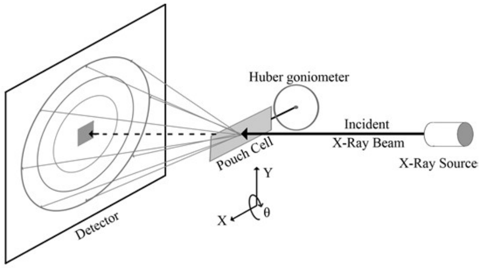


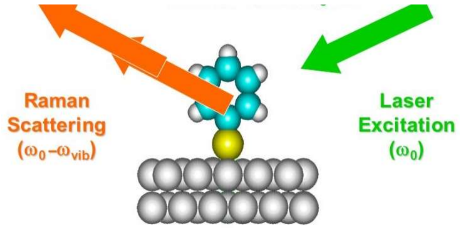
OBJECTIVES

- develop approaches to accurately detect and quantify Li deposition during fast charge conditions
- provide information on Li deposition to XCEL teams to develop methods enabling fast charge

APPROACH

- **Explore and develop several complementary techniques**
  - **what works well and not!**
- X-Ray diffraction & tomography
- Raman Spectroscopy
- Mass Spectroscopy
- Acoustic Analysis
- Feedback to the XCEL teams

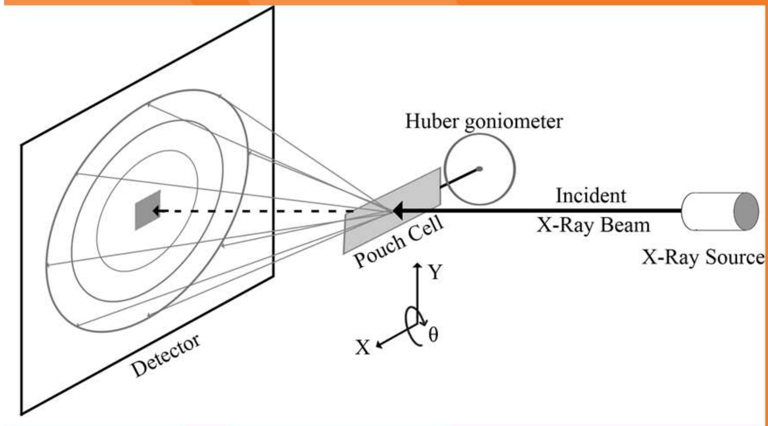




MILESTONES

Li detection related milestones in XCEL

Milestone	End Date	Status
Detect lithium metal deposits using in situ x-ray characterization and correlate results to smart-separator detection data.	6/30/2020	On Track
Preliminary results acquired for each diagnostic tool (tomography, spectroscopy, scattering, impedance spectroscopy, heat transfer)	3/30/2019	Completed
Rationalize performance and degradation experimental findings from NREL, Argonne and Idaho National Labs using models to explain underlying mechanisms behind observed electrochemical performance and degradation	6/30/2019	On Track
Perform initial proof-of-concept experiments to identify the impacts of fast charging at the cell level using non-destructive, in operando techniques including acoustics	3/31/2019	Completed



X-RAY DIFFRACTION & TOMOGRAPHY DETECTION OF LI DEPOSITION

Michael Toney, Johanna Nelson Weker & Hans Georg-Steinrück (SLAC National Acceleratory Laboratory)
Donal Finegan (NREL)

XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries
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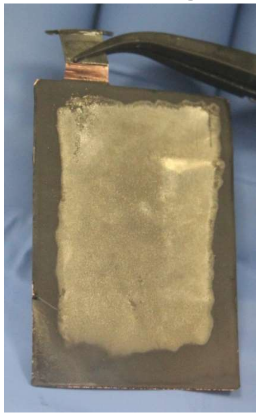
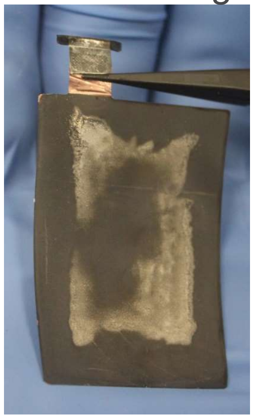
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

Qualitative Measurement of Li Plating

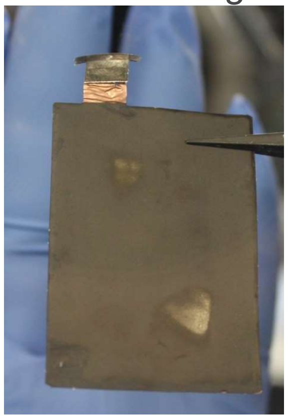
6C - charged



6C - discharged



4C - discharged

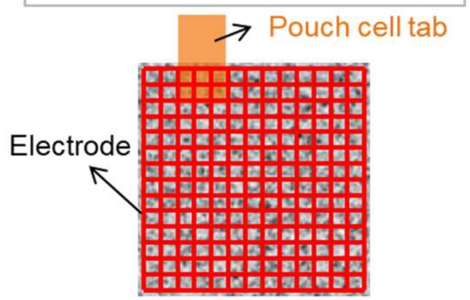


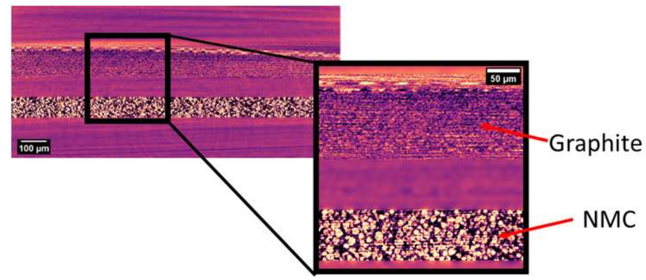
- *Qualitatively*: Different charging conditions → Different electrode conditions after cycling
- How can we ***quantify*** changes spatially within the cell and connect it to loss of cell capacity?

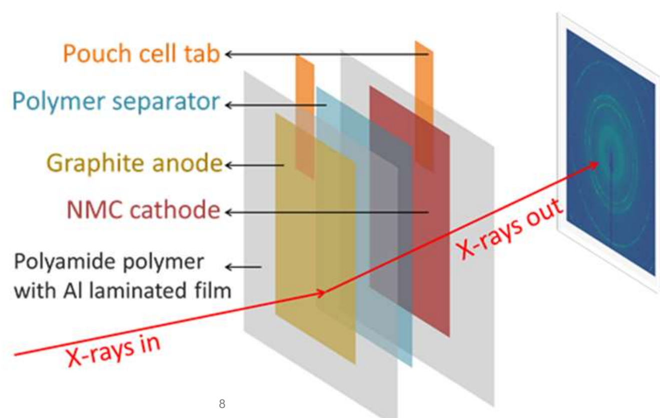
X-ray based Characterization of Single Layer Pouch Cell: spatially resolved XRD and micro-tomography

- Spatially resolved 2D mapping by X-ray diffraction (XRD)
- Micro-tomography (micro-CT) imaging

2D XRD map by rastering







Coupled, Multiscale Approach to Li detection

Electrochemistry:
- *Capacity*
- *Cycling data*

DIFFRACTION

mm

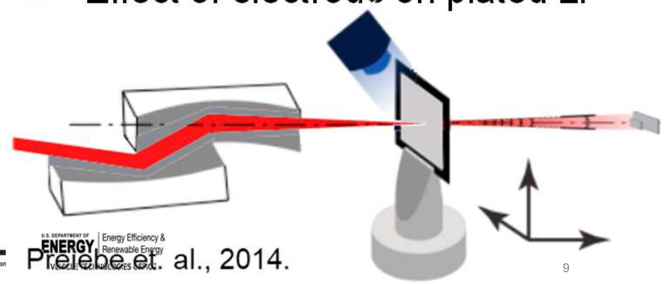
μm

nm

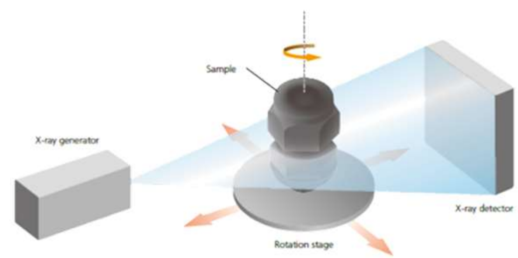
- Macro (mm) scale:
  - 2D map of entire cell
  - Find regions with Li plating
- Micro - submicron scale:
  - Microdiffraction → Li 'cluster size'
  - Depth Heterogeneity of electrode
- Nanoscale:
  - Nanodiffraction → Nucleation of plating
  - Effect of electrode on plated Li

IMAGING

- Microscale
  - Micro-CT on electrode
  - Porosity, tortuosity of electrodes
  - Morphology of plating



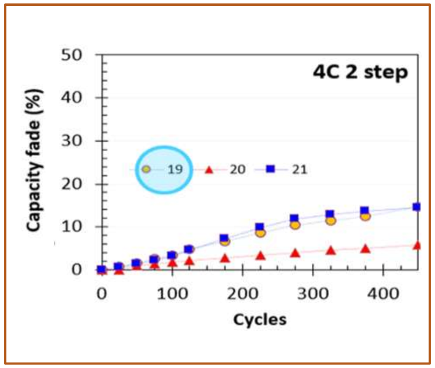
Preiebe et. al., 2014.

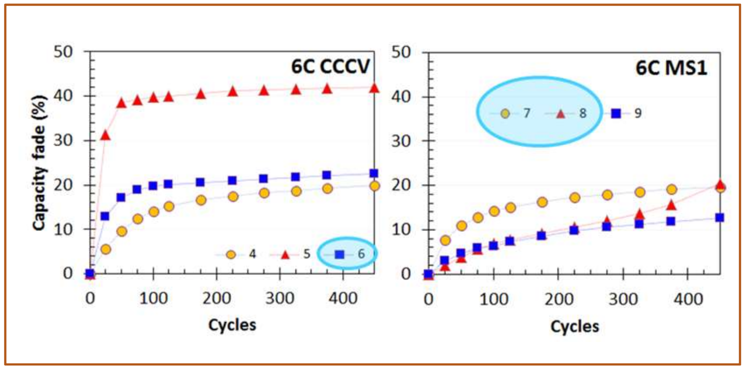


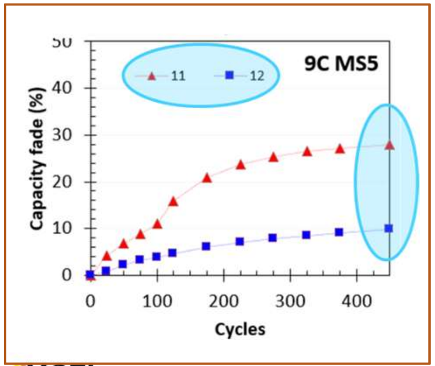
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

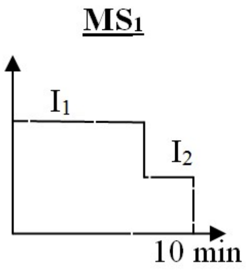
2D mapping – XRD cells cycled at INL

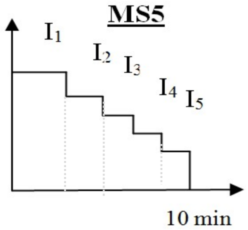
"Round 2" – 3.0 mAh/cm^2
All cells at 10% SOC
Details - BAT383 & 339











Reference cell:

Pristine (Unformed)

XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries
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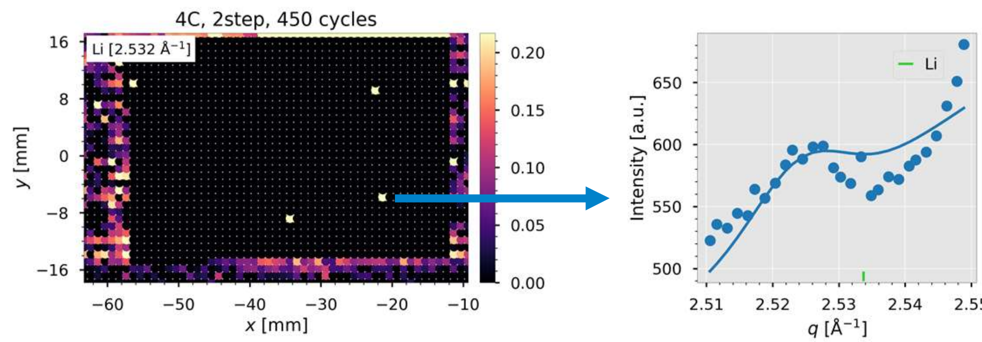
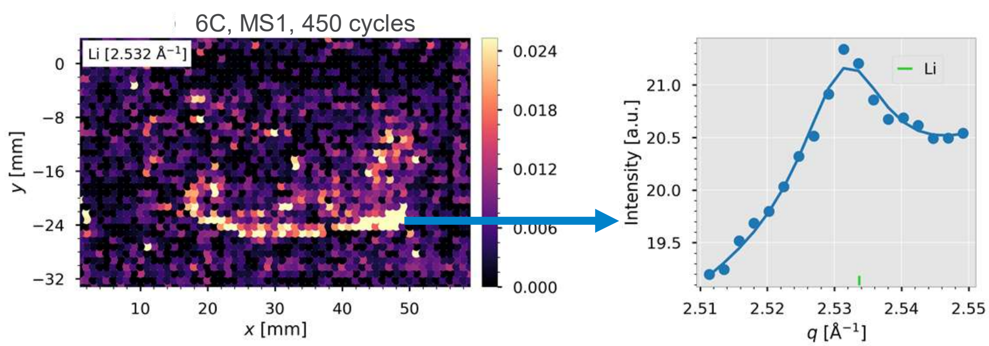
Li Plating Inhomogeneity at the mm-Scale



4C Cycled Cell:
Very Little Li-Plating

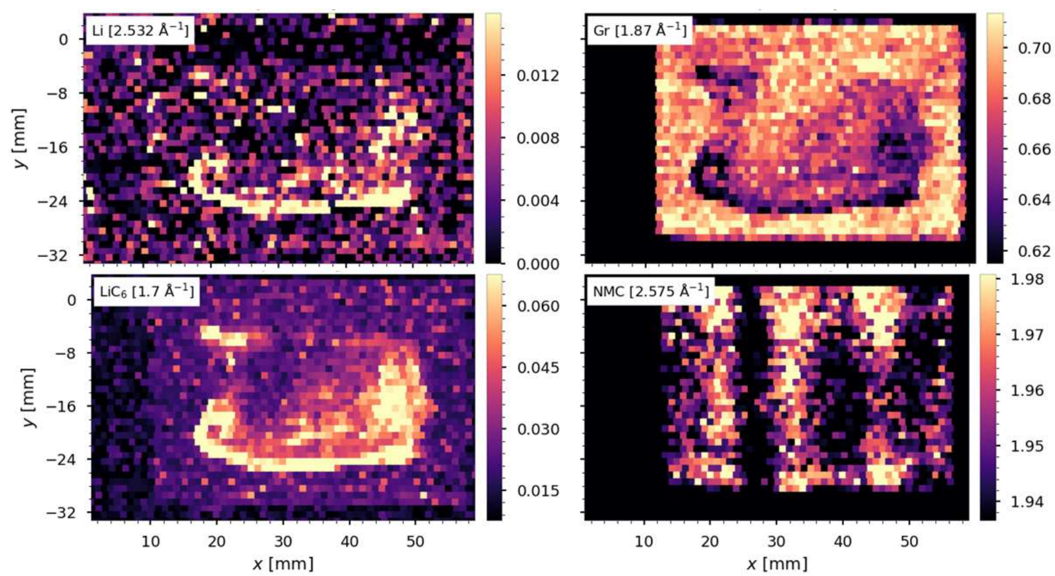


6C Cycled Cell:
Significant Li-Peaks

Lithium Intensity from 110 peak

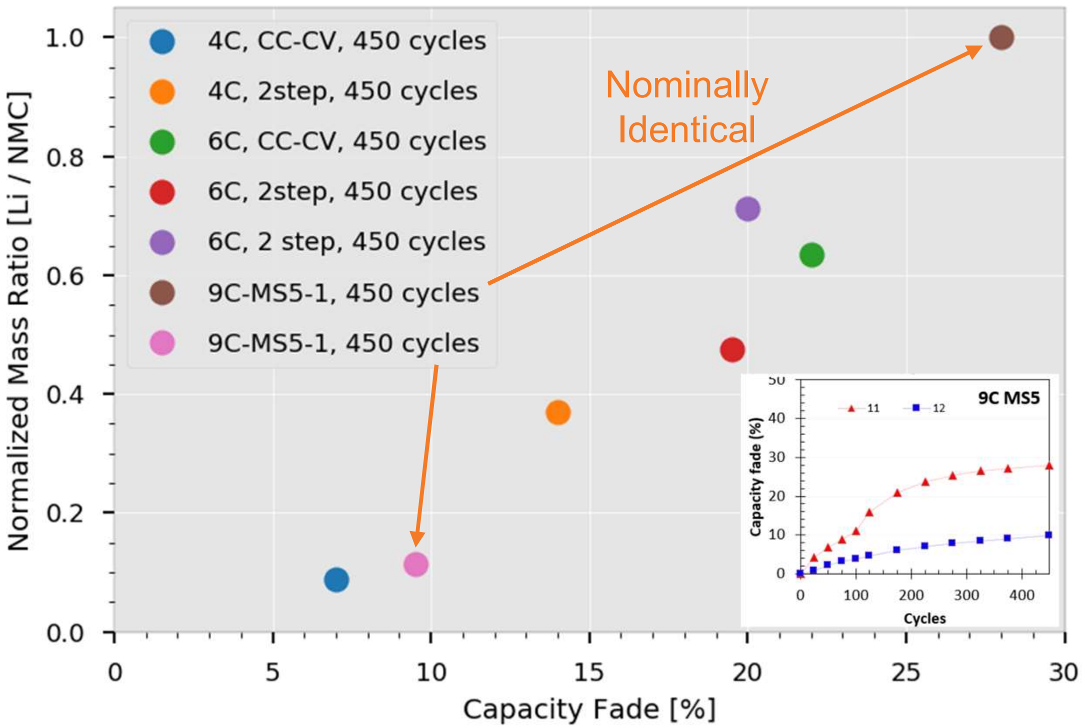
Correlating Li intensity to other Phases at the mm-scale

Cycling: 6C, CCCV, 450 cycles



- Intensities of Li and Gr anti-correlated
- Intensities of Li and LiC_6/LiC_{12} correlated
- NMC shows pattern; no obvious correlation with Li

Li Plating and Capacity Fade at the mm-scale

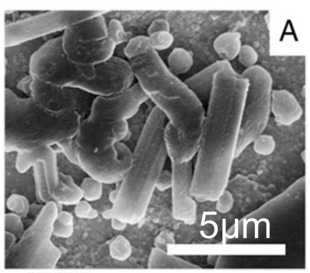


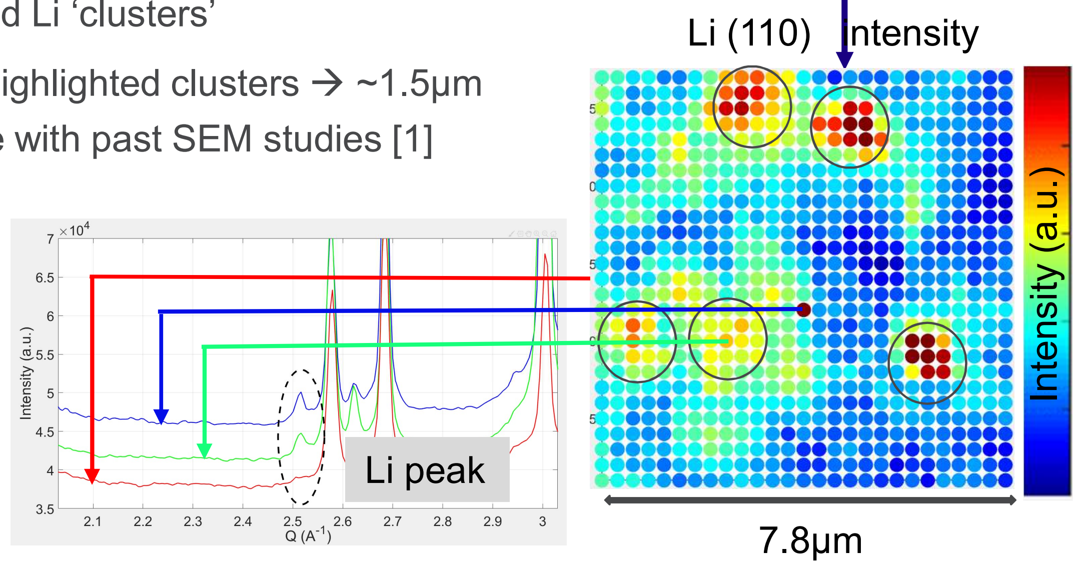
Li heterogeneity at the µm-scale

Round 1 cell (2.0 mAh/cm^2), 100 cycles at 6C

- Mm-scale scans (powder diffraction):
  - Heterogeneities at the full cell level
  - Washes over local (µm-scale) heterogeneities
- µm-scale scans (microdiffraction):
  - Obtain local variations in Li intensity → size of plated Li 'clusters'
- Average size of highlighted clusters → ~1.5µm
  - Comparable with past SEM studies [1]

[1] Feifei Shi et. al., 2017.

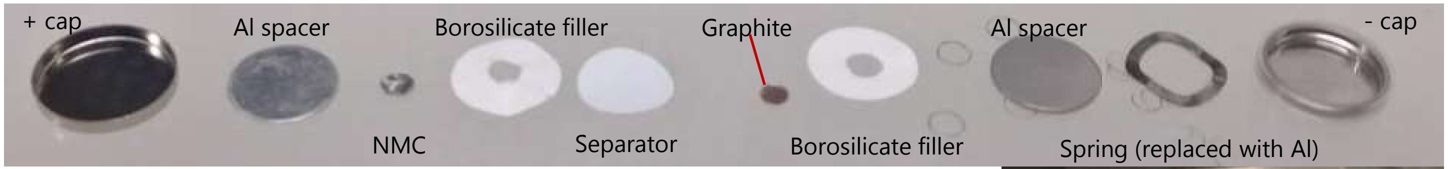


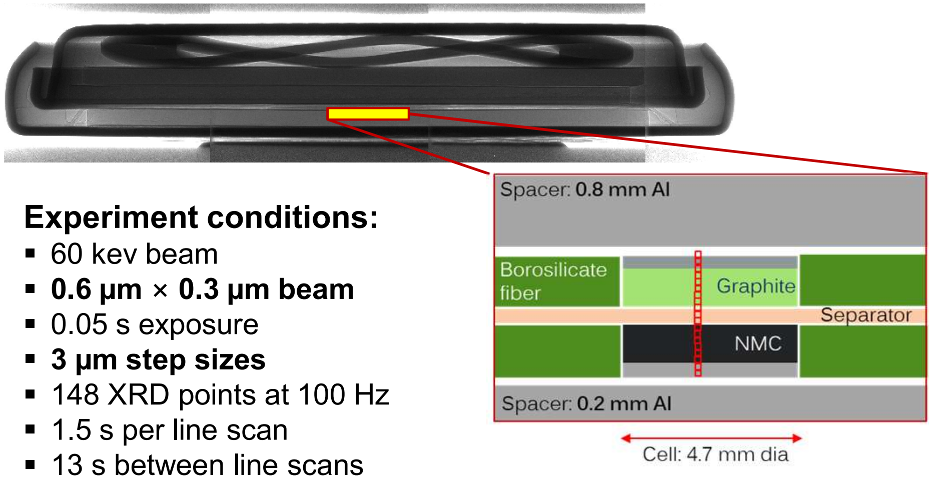


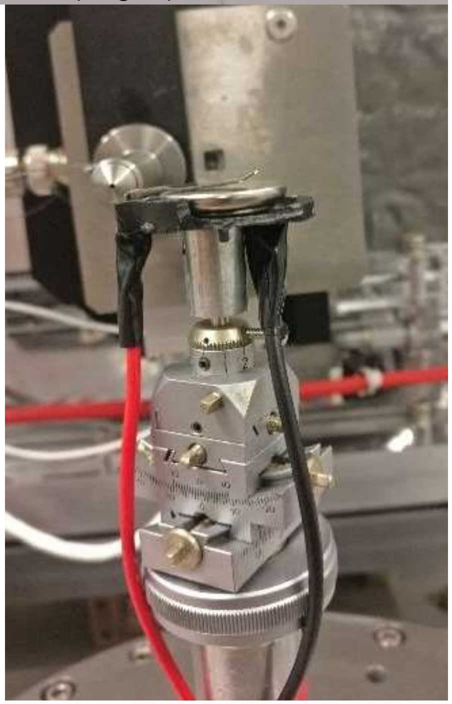
Micro-cell design for *operando* XRD

High speed and high resolution XRD:

- Maximize X-ray transparency and signal/noise ratio
- Minimize performance loss



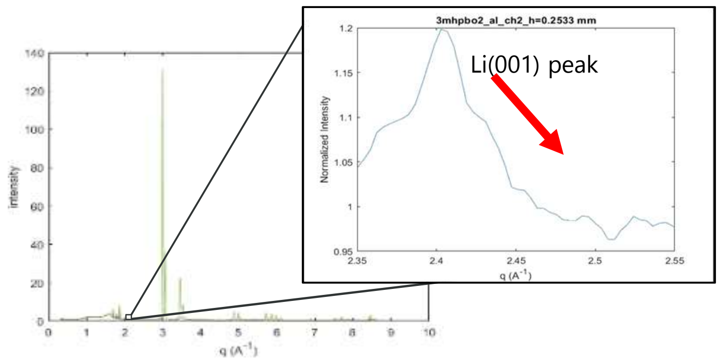


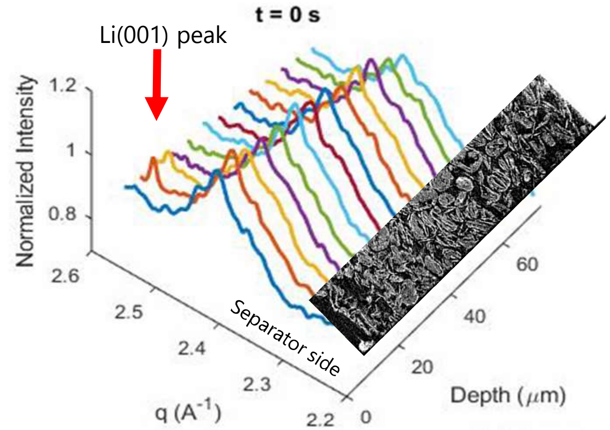


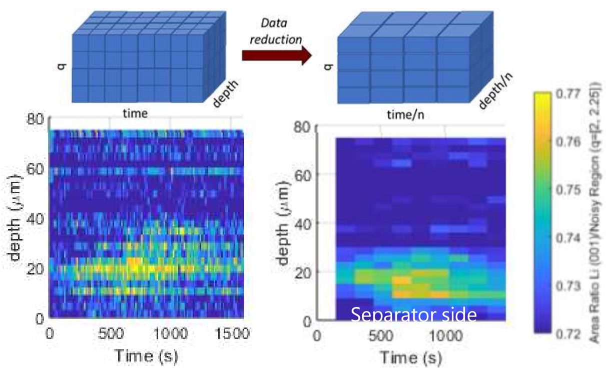
Experiment conditions:

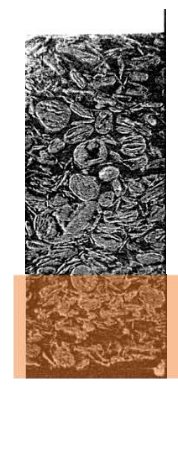
- 60 kev beam
- **0.6 µm × 0.3 µm beam**
- 0.05 s exposure
- **3 µm step sizes**
- 148 XRD points at 100 Hz
- 1.5 s per line scan
- 13 s between line scans

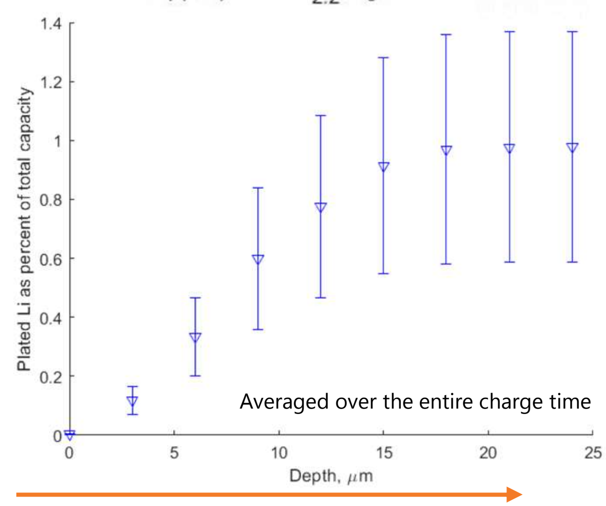
Operando depth-profiling XRD of anode

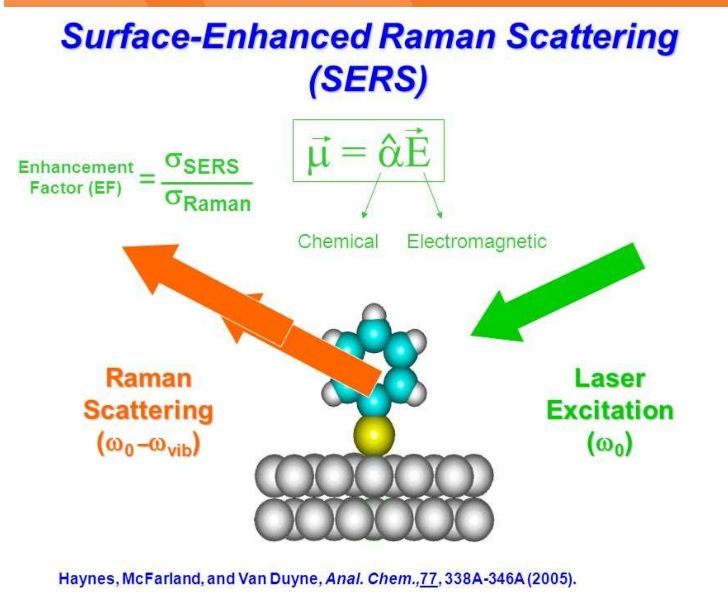










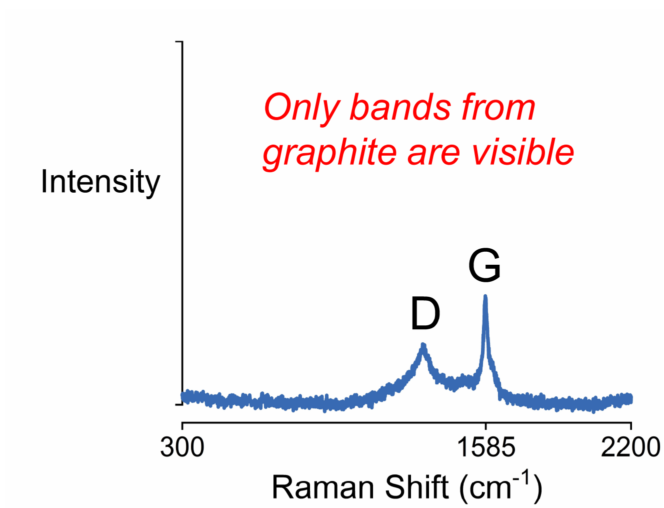


RAMAN SPECTROSCOPY

Daniel Abraham
Argonne National Laboratory

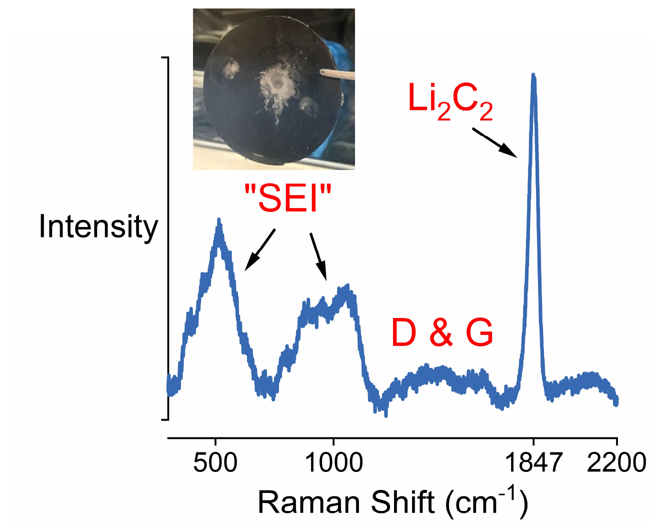
Lithium acetylide band in the Raman spectra of graphite electrodes is a spectroscopic marker for metallic lithium

Graphite electrode from a highly aged cell (360, C/3 cycles, **no Li plating**)



Extensive SEI growth does not produce Raman signals

Graphite electrode after fast charging (6C charge, **Li plating**)



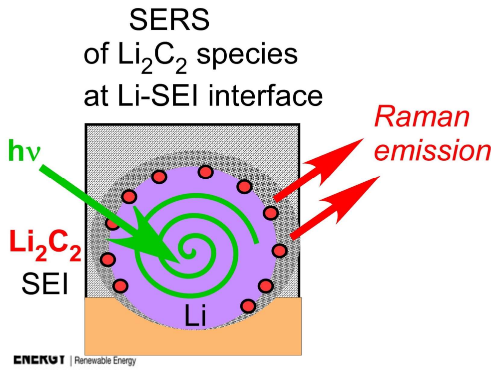
Very intense SEI and acetylide (Li_2C_2) bands are visible in Raman spectra of electrodes containing metallic Li nuclei

Li plating enhances Acetylide (carbide) band

Origin: small carbide clusters form by reduction of SEI species by plated Li, becoming part of its SEI

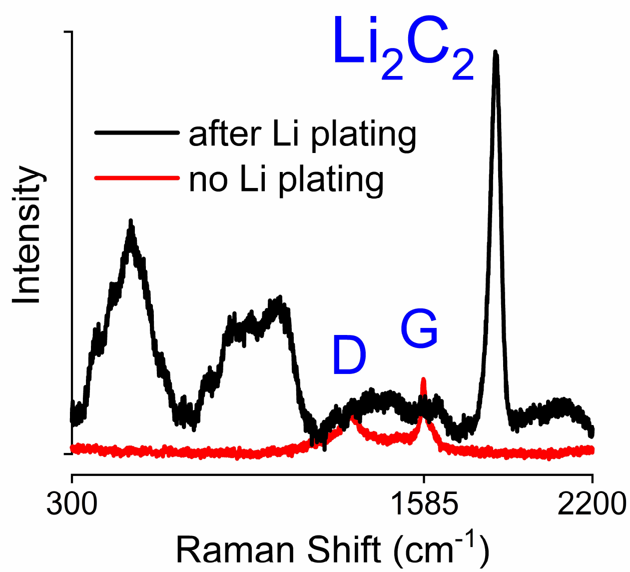
$$\text{SEI or electrolyte} + Li_{(s)} \rightarrow Li_2C_2$$

Mechanism: plated Li enhances the signal from its immediate SEI through surface-enhanced Raman scattering (SERS)



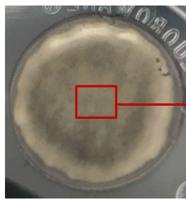
Result: Li_2C_2 band is only detected when metallic Li is present

Sensitive and specific to Li

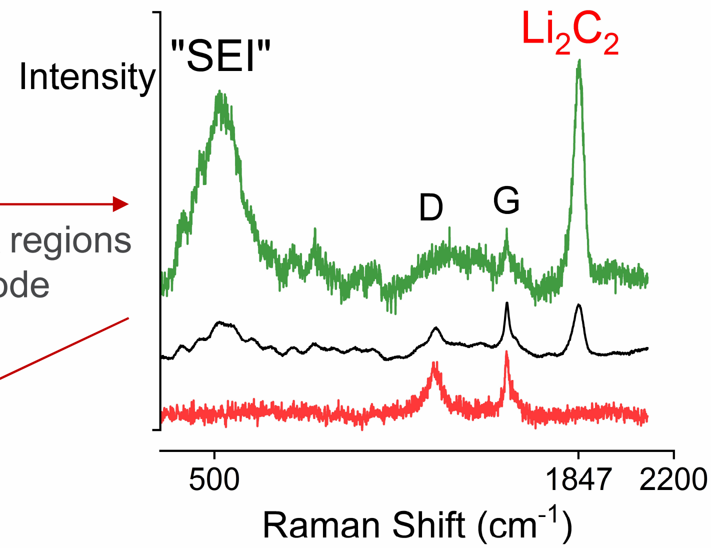


Spatially-resolved detection of plated Li

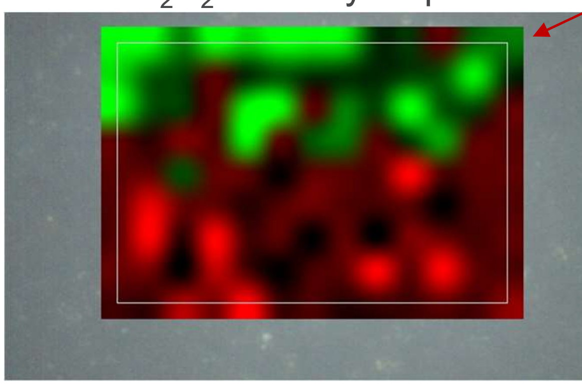
graphite electrode
after 7 cycles at 10C



Measure different regions
of the electrode

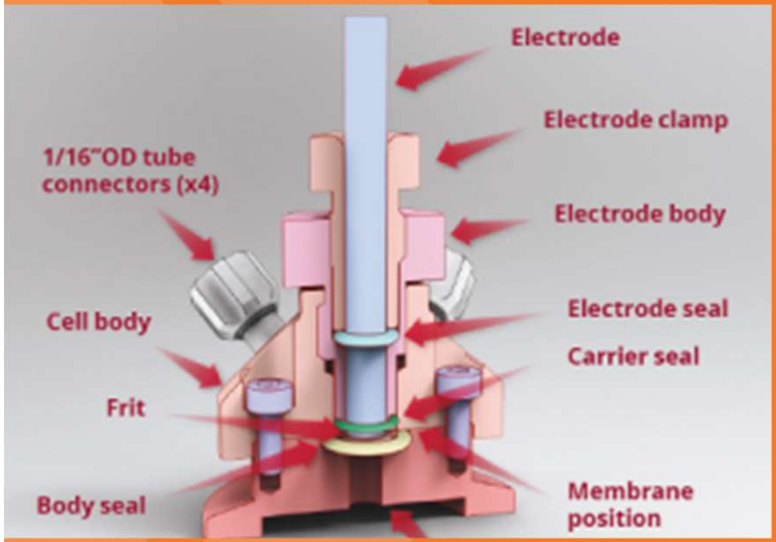


Li_2C_2 intensity map



Raman spectroscopy can be used to obtain a spatial map of plated Li (by detecting Li_2C_2), even when no visual indication of plating exists.

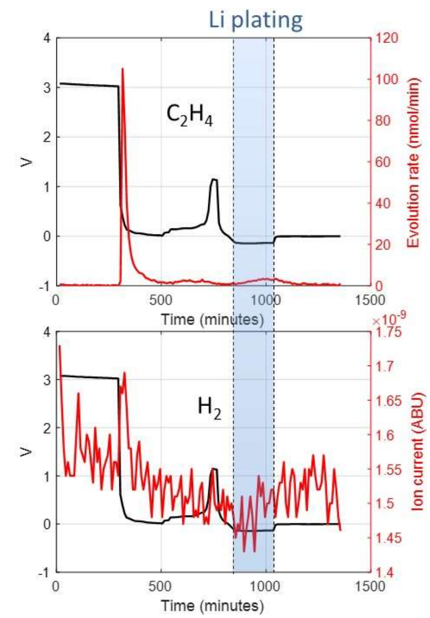
Rodrigues et. al., “Li Acetylide: A Spectroscopic Marker for Li Deposition During Fast Charging of Li-Ion Cells”, ACS Appl. Ener. Mater. 2019, 2, 873−881.



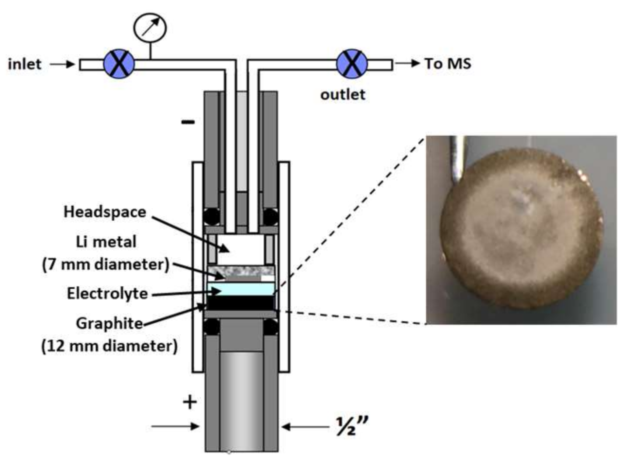
MASS SPECTROMETRY

Bryan McCloskey &
Nitash Balsara (LBNL)

In situ Li plating detection: Does Li plating evolve gases?



Approach: In situ differential electrochemical mass spectrometry



Bottom Line:

- Gas evolution is within detection limits.
- Less than 0.01 mol per mol of Li plated!
- Conclusion is that Li plating will not cause swelling of pouch cells.

XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries
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Ex situ Li plating detection

Procedure

1. **Extract fully delithiated graphite electrodes from cells**
2. **Place in sealed vial, attach to Mass Spec**
3. **Inject H_2O/H_2SO_4, monitor/quantify gas evolution**

Plausible reactions

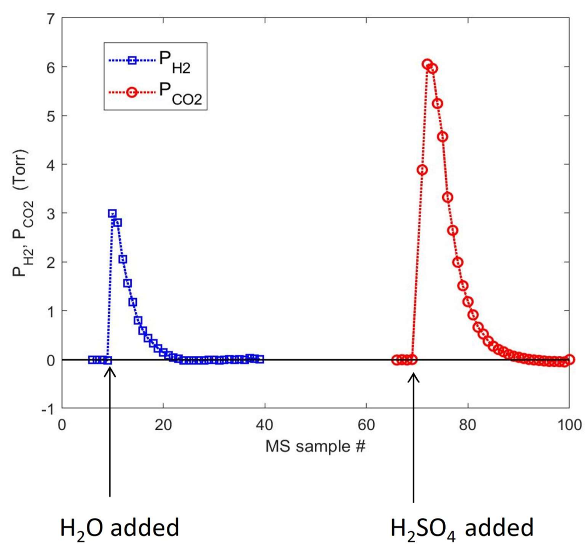
After H_2O addition:

$H_2O + Li(s) \longrightarrow LiOH + \frac{1}{2}H_2$

$H_2O + LiC_6 \longrightarrow LiOH + \frac{1}{2}H_2 + C_6$

After H_2SO_4 addition:

$H_2SO_4 + Li_2CO_3 \longrightarrow CO_2 + H_2O + Li_2SO_4(aq)$

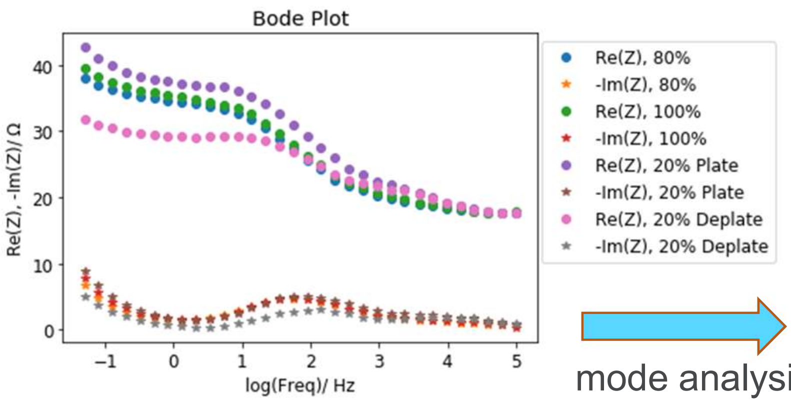


µmol H_2 (Li)	µmol CO_2 ($LiRCO_3$)	Calculated cap. loss (assume 1 e^- per Li)	Cap. loss from cycling data
1.43 (2.86)	4.1 (4.1)	**0.29 mAh**	**0.28 mAh** = (0.23 + 0.03 + 0.02)

Bottom Line: Titration captures all of the Li plated in a composite electrode without interacting with intercalated Li.

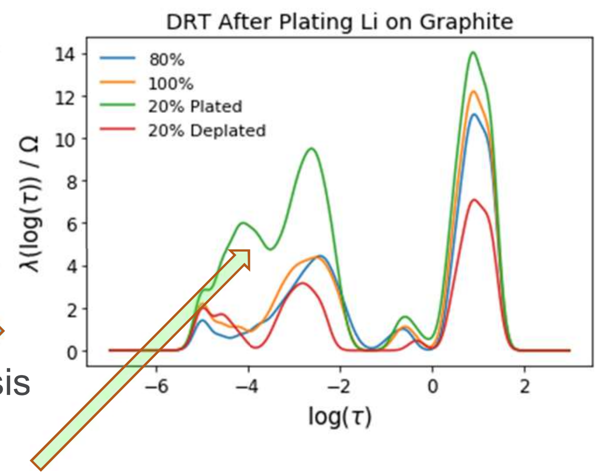
Impedance signatures of Li plating

Raw data as a function of charging (and plating)



mode analysis

Analyzed data – distribution of relaxation times



Unique mode associated with plating

PART D: ACOUSTIC ANALYSIS

Dan Steingart (Princeton)

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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Acoustic Signatures of Li plating

Objectives:
- Look for acoustic signatures of Li deposition in CAMP cells
- Assess non-destructive confirmation routes

Basic Acoustics

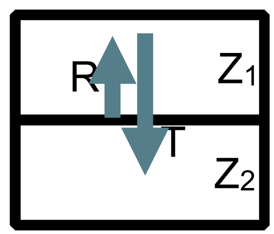
Sound speed

$$c = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}$$

Longitudinal/Shear Modulus
Density

Acoustic impedance

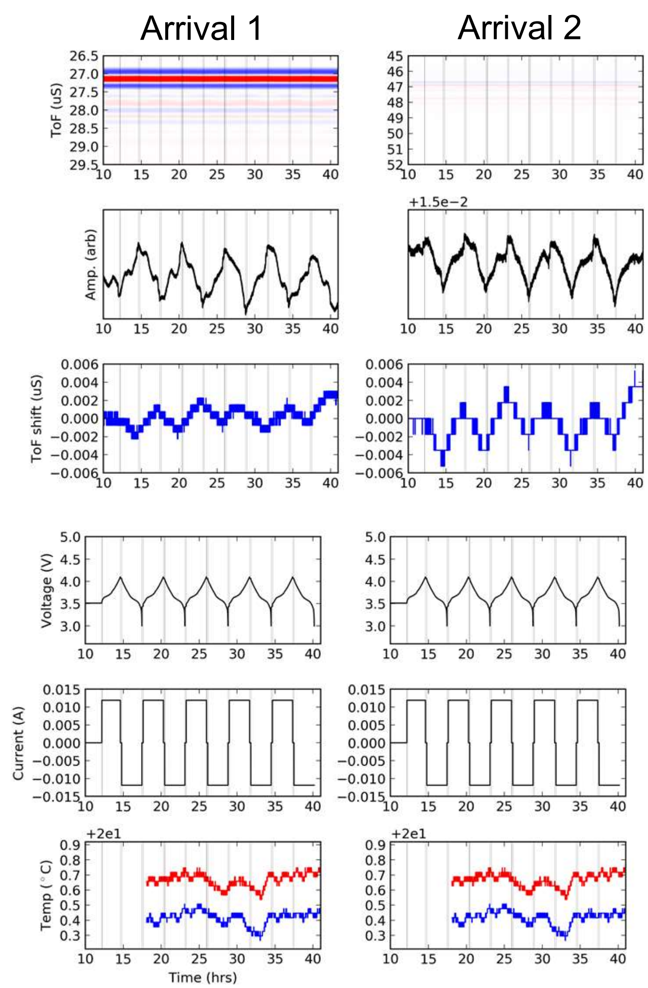
$$Z = \rho \cdot c$$



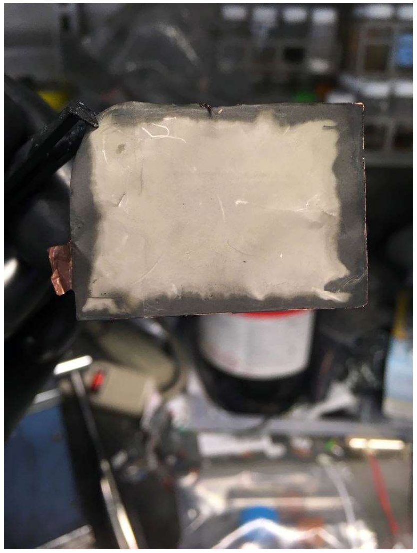
Hypothesis:
Cycling affects the behavior of sound traveling through a battery

GENTLE START

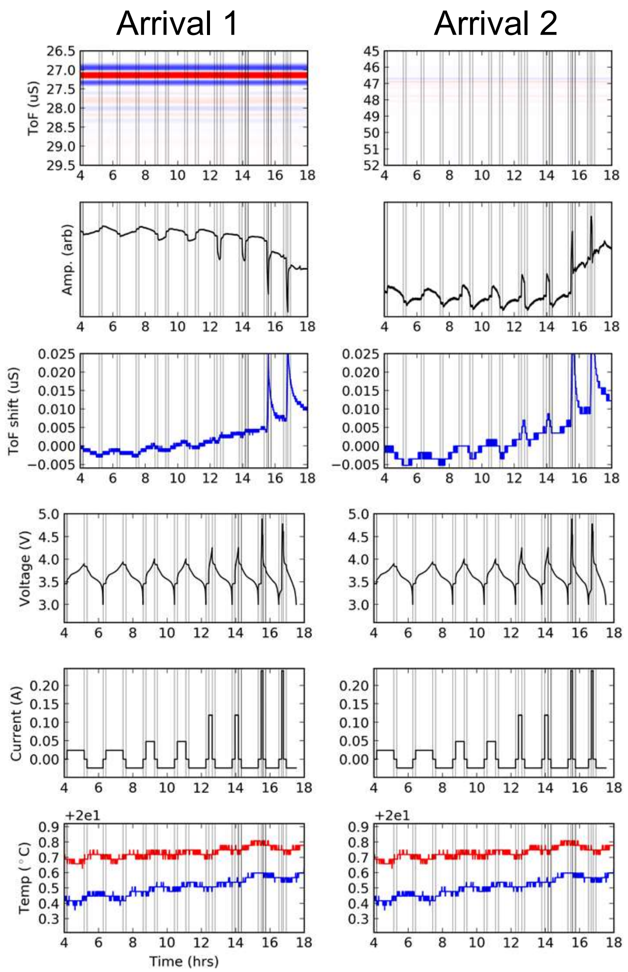
- “Round 2” – 3.0 mAh/cm^2
- C/2 Cycling
- Held at 25˚C (+/- 0.5 ˚C)
- SoC shift as expected at both wave arrivals
- SoH “break—in” shift correlates well with previous work
- No apparent damage



ABUSIVE FINISH

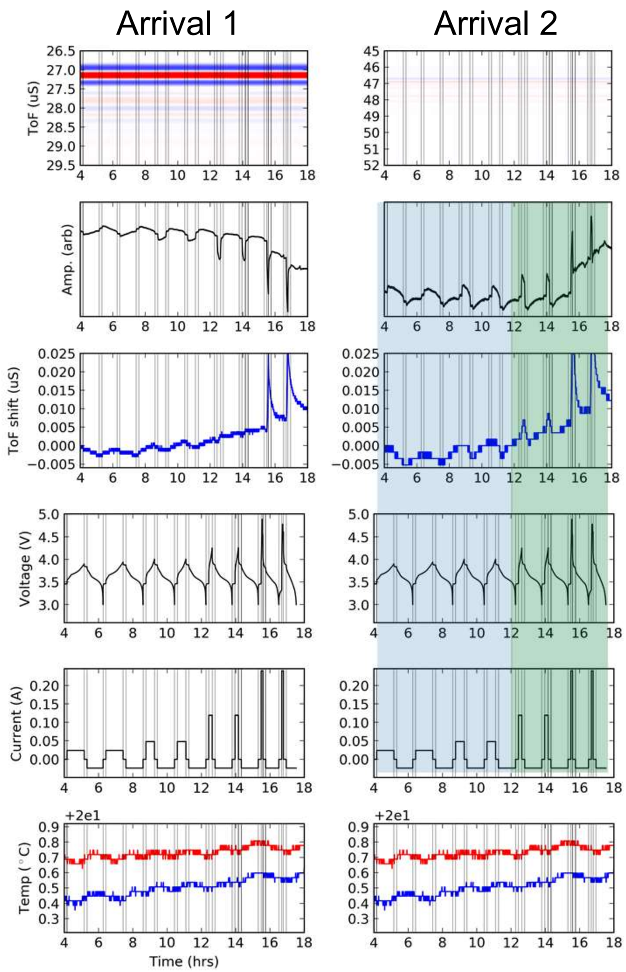


After 10 - 10 C Cycles



ABUSIVE FINISH

- “Round 2” – 3.0 mAh/cm^2
- 1C -> 2C -> 5C -> 10 C
- Held at 25˚C (+/- 0.5 ˚C)
- SoC shift as expected at both wave arrivals at first
- SoH “break—in” shift correlates well with previous work
- **Significant Pattern Shift at 10 C change -> Lithium?**



RESPONSE TO PREVIOUS YEARS REVIEWERS' COMMENTS

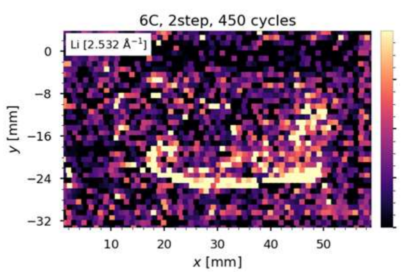
Not previously reviewed

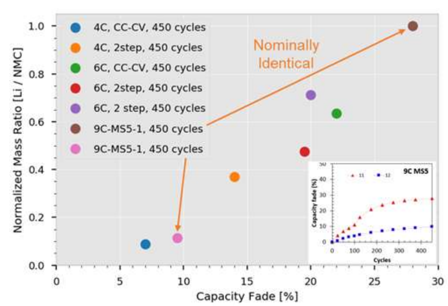
COLLABORATION ACROSS LABS AND UNIVERSITIES

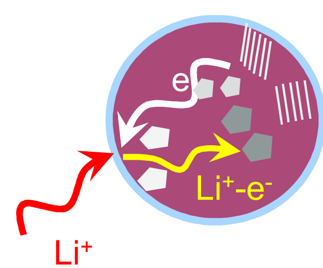
- Five national laboratories (Argonne, NREL, INL, SLAC, and LBNL) and three universities (Stanford, UC-Berkeley, and Princeton) have teamed to form this integrated effort focused on enabling fast charge capability.
- National User Facilities involved in this work presented include the Advanced Photon Source, & Stanford Synchrotron Radiation Lightsource. International Facilities include the European Synchrotron Radiation Facility.
- This effort is part of a broad range of unified studies (BAT338, BAT339, BAT340, BAT 341, BAT371, BAT383, BAT384, BAT386).

REMAINING CHALLENGES AND BARRIERS

- What SOC does Li plating start; dependence on charge rate/profile?
- What are initiation sites of Li plating (e.g., edge vs basal)?
- Establish detection limits & quantification for Li plating
- What dictates observed heterogeneity in Li plating?
- Find solutions!

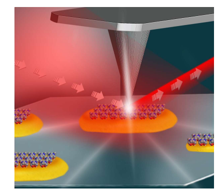




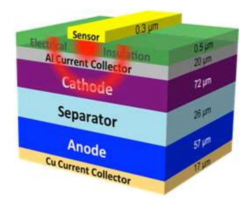


FUTURE WORK

- Transition to *Operando* Measurements
  - ❑ At what SOC does Li plating start; dependence on charge rate/profile?
  - ❑ XRD, Raman Spectroscopy - Li-plating (Li-acetylide) detection on graphite
  - ❑ Correlate results to micro-tomography to 2D & 3D XRD & develop unique anode and cell design to enable high resolution imaging



- Quantify amount of plated Li → relate to capacity lost
  - ❑ Impedance - assess sensitivity
  - ❑ Acoustic Analysis - refine approach to increase sensitivity
- Understand spatial heterogeneity
  - ❑ What dictates observed heterogeneity in Li plating?
  - ❑ 3D XRD → depth resolution & surface layers of Li
  - ❑ Operando Optical Video Microscopy

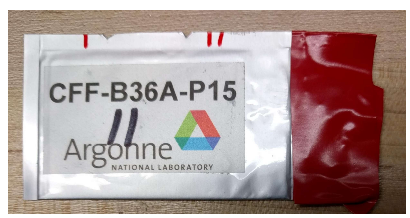


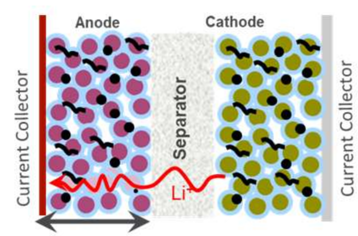
- What are initiation sites of Li plating (e.g., edge vs basal)?
  - ❑ Near-field FTIR - model electrodes - if plating occurs on graphite planes or edges
- Temperature increases
  - ❑ Thermal Signatures of temperature increases - 4 sensors integrated into full cells.
  - ❑ “smart” trilayer separator & RTD

Any proposed future work is subject to change based on funding levels.

SUMMARY

- Explore and develop complementary techniques for Li detection - what works well and not!
- Develop methods to directly detect and characterize (2D and 3D space and time) Li metal plating during fast charging
    - Spatial Inhomogeneities in Li-plating over a range of length scales from: microns to mm
    - Initial quantification of Li-plating extent - correlate with capacity fade (qualitative)
    - Spatial correlation between Li-Plating & graphite staging





XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

CONTRIBUTORS AND ACKNOWLEDGEMENTS

Aashutosh Mistry
Andy Jansen
Abhi Raj
Alison Dunlop
Andrew Colclasure
Antony Vamvakeros
Aron Saxon
Bryan McCloskey
Bryant Polzin
Chuntian Cao
Daniel Abraham
Daniel Steingart
Dave Kim
David Robertson
David Wragg
Dean Skoien
Dennis Dees
Donal Finegan
Eongyu Yi
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Francesco De Carlo
Guoying Chen
Hakim Iddir
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Matt Keyser
Michael Evans
Michael Toney
Nancy Dietz Rago
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Pierre Yao
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Ren Yang
Robert Kostecki
Ruqing Xu
Ryan Jackman
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Sangwook Kim
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Seoung-Bum Son
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Shriram Santhanagopalan
Steve Trask
Tanvir Tanim
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Venkat Srinivasan
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Vince Battaglia
Vivek Thampy
Wei Tong
Weijie Mai
Wenxiao Huang
William Huang
Yanying Zhu
Yi Cui
Zhenzhen Yang

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XCEL

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VEHICLE TECHNOLOGIES OFFICE

Argonne NATIONAL LABORATORY

SLAC NATIONAL ACCELERATOR LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB Lawrence Berkeley National Laboratory

INL Idaho National Laboratory

TECHNICAL BACKUP SLIDES

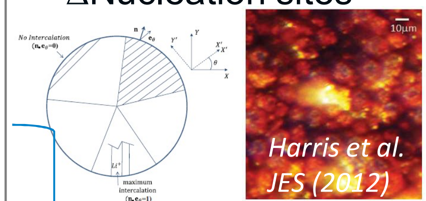
Multiscale Phenomena

length scale		*heterogeneity*
0.1μm	Grain	Crystal anisotropy; Particle-to-particle contact
1μm	Particle	Particle size, morphology; Electrolyte transport limitation leads to plating at electrode surface
10μm	Electrode thickness	
100μm	Electrode coating	Porosity/tortuosity variation; Anode overhang; Electrode misalignment; Electrolyte shorting
1mm	Edge effects	
1cm	Cell	Dry out, delamination; Pressure; Temperature; Tab configuration
10cm		

Main focus: Particle size, morphology; Electrolyte transport limitation leads to plating at electrode surface; Porosity/tortuosity variation

examples

ΔNucleation sites

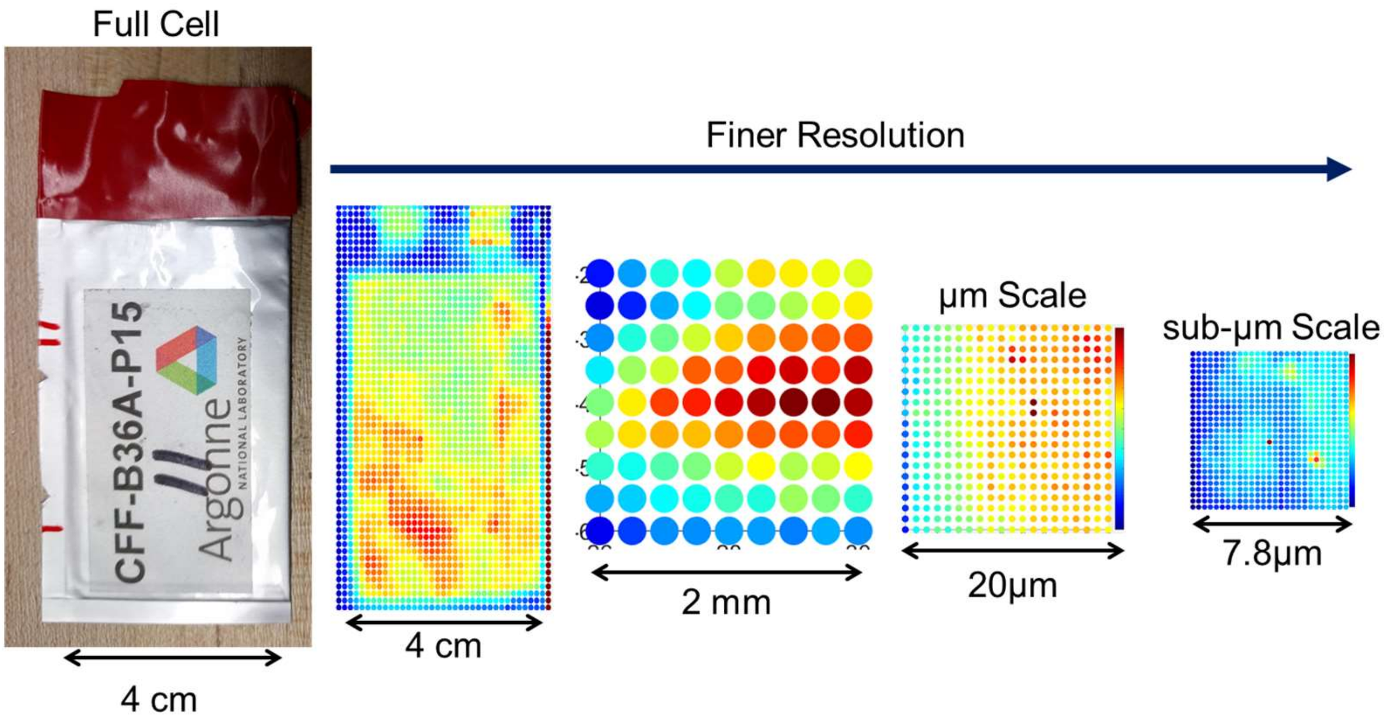


Harris et al. JES (2012)

Cell-scale heterogeneities

Ira Bloom (ANL)

TECHNICAL BACKUP SLIDES



- Characterization of heterogeneity of Li plating at multiple length scales
- Fast data acquisition at synchrotron allows *in-situ/operando* measurement

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TECHNICAL BACKUP SLIDES

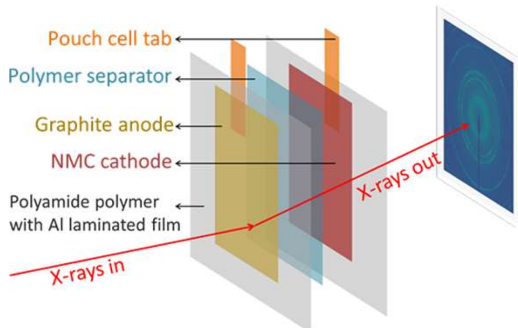
Anode:

- ~3.0 mAh/cm^2
- Foil (Cu) thickness:10µm
- Electrode Thickness: 80µm
- Porosity: 34.5%

Cathode:

- ~2.7 mAh/cm^2
- Foil (Al) thickness:20µm
- Electrode Thickness: 91 µm
- Porosity: 35.4%

Single layer pouch cell



Composition (wt%):

- 91.83% Graphite
- 2% Timcal C45
- 6% PVDF
- 0.17% Oxalic acid

Composition (wt%):

- 90% NMC532
- 5% Timcal C45
- 5% PVDF

Special thanks to: Andy Jensen, Ira Bloom, Eric Dufek, CAMP and XCEL teams

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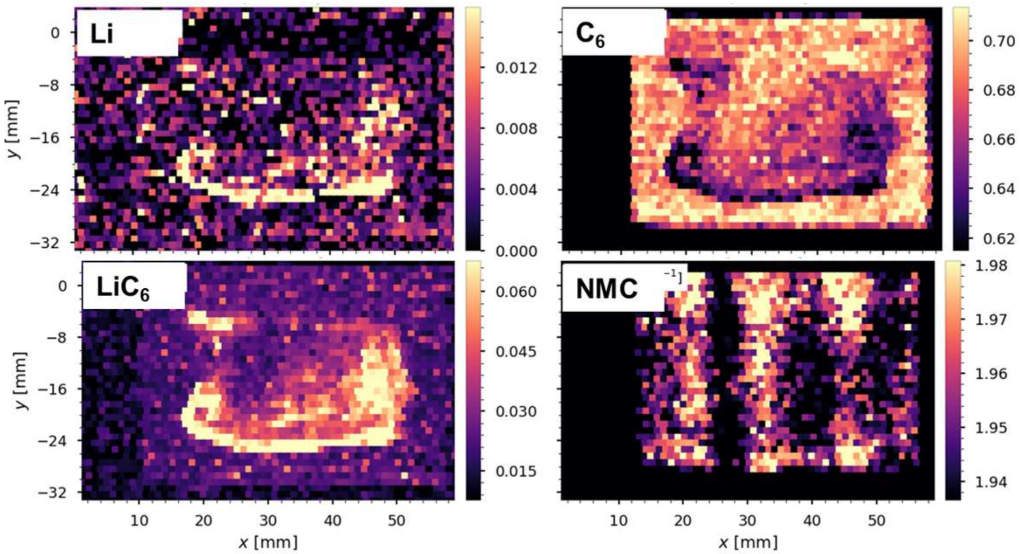
TECHNICAL BACKUP SLIDES

Correlating Li-Plating to other Phases

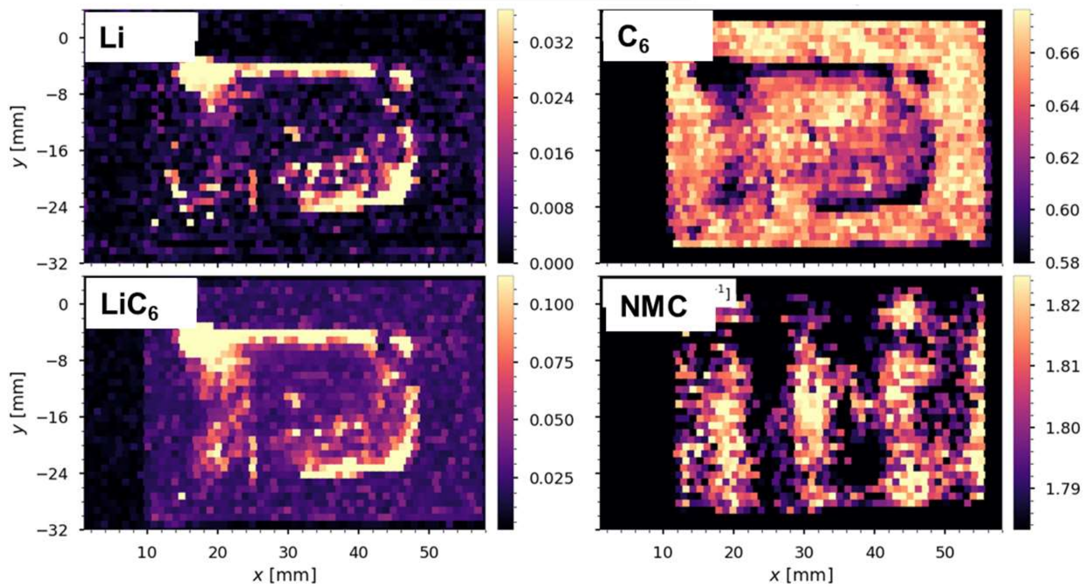
6C, CCCV, 450 Cycles



- Intensities of Li and Gr Anti-Correlated
- Intensities of Li and LiC_6/LiC_{12} Correlated
- NMC shows Patterns but no Obvious Correlation with NMC

TECHNICAL BACKUP SLIDES
Correlating Li-Plating to other Phases

9C, MS5, 450 Cycles



- Intensities of Li and Gr Anti-Correlated
- Intensities of Li and LiC_6/LiC_{12} Correlated
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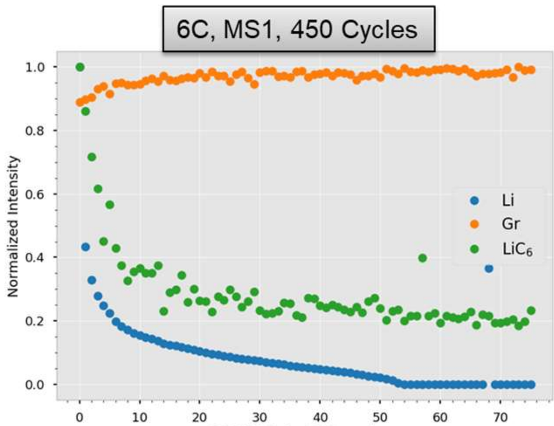
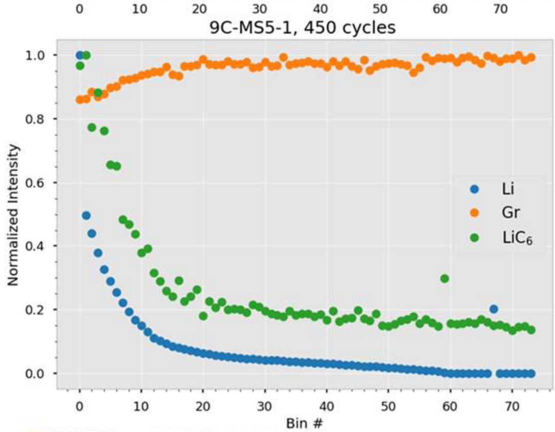
TECHNICAL BACKUP SLIDES

Another look at Phase Correlations





- Intensities of Li and Gr Anti-Correlated
- Intensities of Li and LiC_6/LiC_{12} Correlated
- No Obvious Correlation with NMC

What leads to this spatial inhomogeneity?

Porosity / Tortuosity / Texture / Cracks ...?

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